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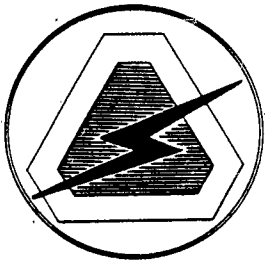
INITIAL ATTEMPTS TO DEVELOP CIRCUIT DEVICES USING SILVER IODIDE AS A SOLID IONIC CONDUCTOR

H. Paul Zeiger



June 1963

UNITED STATES ARMY
ELECTRONICS RESEARCH AND DEVELOPMENT LABORATORY
FORT MONMOUTH, N.J.

U. S. ARMY ELECTRONICS RESEARCH AND DEVELOPMENT LABORATORY

FORT MONMOUTH, NEW JERSEY

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INITIAL ATTEMPTS TO DEVELOP CIRCUIT DEVICES USING SILVER IODIDE AS A SOLID IONIC CONDUCTOR

H. Paul Zeiger

DA Task No. 3A99-25-003-01

Abstract

In an effort to develop all-solid ionic devices capable of application to electronic circuits it was found necessary, because ionic flow involves a simultaneous flow of charge and atomic mass, to study electrode processes occurring at solid electrolyte/solid electrode interfaces. It was found that relatively simple diffusion and concentration cell effects operate and that logical models can be postulated to explain the observed experimental data. Generally speaking, nearly every device that was tried (memory and time-delay devices) behaved roughly as expected. No immediate practical utility is envisioned for any of these.

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CONTENTS

FIGURES

INITIAL ATTEMPTS TO DEVELOP CIRCUIT DEVICES USING SILVER IODIDE AS A SOLID IONIC CONDUCTOR

I. INTRODUCTION

It is well-known that certain solid salts can conduct electricity substantially solely by transport of ions rather than by the more conventional transport of electrons. Solid silver iodide is an example of such an ionic conductor. It is of particular interest because:

1. It exhibits no significant transport of either electrons or iodide ions and it can be assumed that all observed current flow is due to the transport of silver ions.

2. Its room-temperature conductivity is relatively high compared to that of other solid ionic conductors.

3. The conductivity of compressed pellets of silver iodide can be altered by appropriate preparation or pretreatment of the original uncompressed powder.

4. Stable and reversible amalgamated silver electrodes are available for simple dc measurement and utilization of the ionic conductivity.[1]

The objective of this work was to make a preliminary evaluation of the possibility that basic circuit components can be built using this flow of silver ions through pellets of compressed silver iodide powder.

It was, of course, appreciated from the very start that ionic flow has two consequences; i.e., a transport of charge and a transport of matter. This is commonplace to the electrochemist but to the electronic engineer it means, to give a crude but illuminating example, that soldered joints migrate through the circuit as a function of current flow.

Such transport of matter as an inevitable adjunct of transport of charge can be viewed, with considerable justification, as a disastrous shortcoming. More optimistically, it can be considered as a sort of second degree of freedom which, if properly turned, may permit us to accomplish a multiplicity of objectives with a single transport of charge. It should be recalled that biological systems invoke this dual transport concept.

Although the device applications described here cannot be considered as spectacular or a threat to conventional electronic components, it is felt that they may be of some interest. They do give a glimpse of the possibilities (and limitations) of an as yet little explored field of endeavor. Also, it is hoped that the work may be of value to those seeking more insight into the general field of ionic processes in solids.

II. IONIC MEMORY DEVICES

Consider an array of the type shown in Fig. 1. Application of a positive voltage to the amalgamated silver electrode will plate a "readin" charge of silver metal onto the platinum. This charge can be stored for eventual readout by reversing the voltage. Such a memory device has been built and was found to work as expected, provided the input voltage exceeded 0.14 volt. Typical results at voltages exceeding 0.14 volt are shown in Fig. 2. We interpret the shaded area in the readout as representing silver which was plated out onto the platinum, but which was not available for subsequent return. A logical model is that the silver plates out in the form of "trees," the "roots" of which plate back first, leaving their "branches" isolated and without electronic contact to the platinum. It is felt that the magnitude of the shaded area could be diminished significantly by appropriate choice of pellet compression conditions and by suitable pretreatment of pellet and platinum surfaces.

At constant applied voltage below 0.10 volt, the initial readin plating current and the reverse readout current take the form of transients as shown in Fig. 3. We propose the following explanation. As pointed out above, in order to deposit silver onto the platinum, it is necessary for the growing silver tree to displace the solid iodide, probably by fracturing it along grain boundaries. Such fracture occurs at voltages exceeding 0.14 (which may be considered as a measure of the mechanical strength of the particular pellet) and silver trees grow. At voltages less than 0.14 the electrical driving force is not great enough to cause gross pellet fracture. Therefore, when a "low-voltage" silver ion arrives at the platinum surface it piles up as a layer which can be dissipated only by diffusion of silver into the platinum. On this basis, the behavior of the array at low voltages should be diffusion-controlled and the diffusion current of silver into platinum should be given by:

$$J = FC_p\sqrt{D/\pi}\, xt^{-\frac{1}{2}} \qquad (1)$$

Where: J = diffusion current
F = Faraday's constant
C_p = concentration of silver at the surface of the platinum
D = diffusion constant of silver into platinum
t = time.

The important feature of Eq. (1) is the inverse square-root relationship between current and time. The experimental curves of Fig. 4 show that log of current is substantially linear with log of time with negative $\frac{1}{2}$ slope as predicted by Eq. (1).

As silver ions diffuse into the platinum the array will begin to exhibit a behavior approaching that of a concentration cell in which one electrode is platinum containing dissolved silver at a concentration C_p

and the other electrode is mercury containing dissolved silver at a concentration C_m. The voltage of such a concentration cell will be given by:

$$C_p = C_m \exp(-eE/kT) \qquad (2)$$

Where: E = voltage of concentration cell.

The value of C_p will be given by:

$$Q = eNvC_p \qquad (3)$$

Where: Q = total charge transport associated with diffusion of silver into the platinum
N = Avogadro's number
v = volume of the platinum electrode.

It follows that:

$$Q = eNvC_m\exp(-eE/kT). \qquad (4)$$

Lumping e, N, v and C_m into a single constant, m, and computing that e/kT at room temperature has a value of 38.9, we have:

$$Q = m\exp(-38.8E). \qquad (5)$$

Equation (5) states that the concentration cell voltage E will be a function of the charge Q transported (by diffusion) into the platinum. It is obvious that we can use the charge pumped into the platinum as our readin and the voltage E as our readout. The readout would, in principle, be nondestructive since high impedance voltage measurements could permit readout without significant disturbance of the readin charge Q.

It can be shown that the working equation for such a nondestructive readout device is given by:

$$\log (Q_t-Q_o) = b-\log(e^{-38.9E}-c) \qquad (6)$$

where Q_o and b are constants and c is experimentally equal to 1.155. We thus have, if we are correct that straightforward electrochemical principles are involved, that a log-log plot of the quantity (Q_t-Q_o) against $(e^{-38.9E}-1.155)$ should be a straight line of unit (45°) positive slope. The points of Fig. 5 represent observed data while the dashed line is drawn to have unit slope. The satisfactory fit indicates the substantial validity of the model.

Despite these encouraging results in that both the destructive and nondestructive readout memory devices behaved as predicted, we cannot become enthusiastic about their utility at this time. The major drawback is that readin and readout times are unpleasantly long.

III. AN IONIC TIME-DELAY DEVICE

Consider the array shown in Fig. 6. Close S_2 so that P is positive with respect to A_2. In a short time the concentration of silver in P and A_2 will adjust themselves to yield a concentration cell voltage equal and opposite to B at which time no further current will flow in Circuit 2. Now close S_1: Silver ions will flow steadily from A_1 to the left face of P and will then diffuse into P. This diffusion into P upsets the concentration-cell balance previously existing between P and A_2 and current will flow in Circuit 2. There will be a time delay between closing S_1 and flow of current through Circuit 2, this delay being dependent upon the time required for a significant number of silver atoms to diffuse through P.

Such a device has been built and found to behave as predicted. The device may be of value in a study of diffusion phenomena; for example, silver through various metals at various temperatures.

IV. AN INTERESTING EXPERIMENT WITH SILVER SULFIDE

A pellet of compressed silver sulfide was placed between platinum electrodes and a small dc voltage applied. The curve relating observed current to applied voltage is shown in Fig. 7.

After we plotted the solid line, the cell adopted the reversible behavior indicated by the dashed line. Upon standing for several hours, the solid-line behavior returned. This curious effect may possibly be explained as follows: We assume that silver sulfide is normally an electronic conductor and an ionic insulator. If the applied electric field disorders the structure, a small ionic component of conduction appears and this interacts strongly with the electronic component. In the above experiment, the rising solid-line curve represents the electronic component. At 0.18 volt the applied voltage is sufficient to dislodge some of the silver ions from the normally ordered silver sulfide lattice, introducing disorder and with it an ionic component of conduction. Since the voltage is assumed to be insufficient to plate out the silver, these movable ions pile up in a cloud at the negative electrode, thus setting up a reverse field which greatly reduced the electronic current. Upon standing, the silver ions again take up order positions and the electronic current is no longer blocked by ionic pile-up.

V. CENTRIFUGING EXPERIMENTS

Since ions are, relative to electrons, rather massive bodies, it should be possible to move them more readily using centrifugal force imposed by a centrifuge. This was tested experimentally, using a cell which resembled that of Fig. 1 except that both electrodes were silver amalgam. Intuitively, it would seem that in the absence of a closed

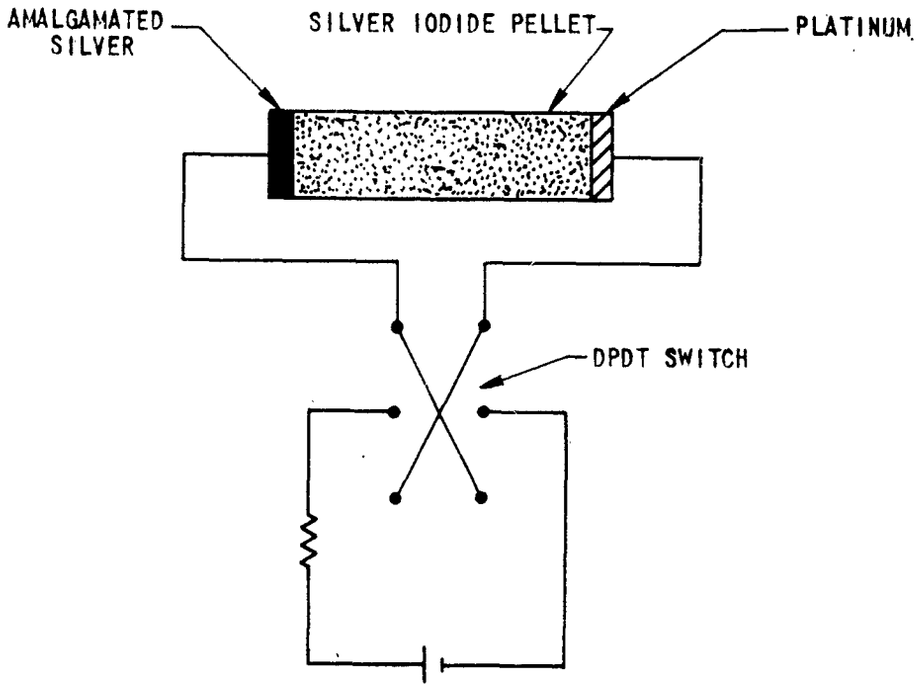
external circuit, the more mobile silver ions would pile up on the outermost electrode until their accumulated field is sufficient to repulse additional ions. This would produce a voltage differential between the electrodes. This voltage was observed experimentally. As expected, it varied as the square of the speed of the centrifuge. However, the magnitude of the voltage was about five times greater than that predicted by a simple force-balance calculation ($eE = mg$). Even so, the generated voltages were measured in tens of microvolts; a level which is inconveniently low for any obvious practical application.

VI. ACKNOWLEDGMENT

The author is greatly indebted to Dr. J. N. Mrgudich for encouragement and assistance and to Dr. F. Kornfeil for numerous illuminating discussions.

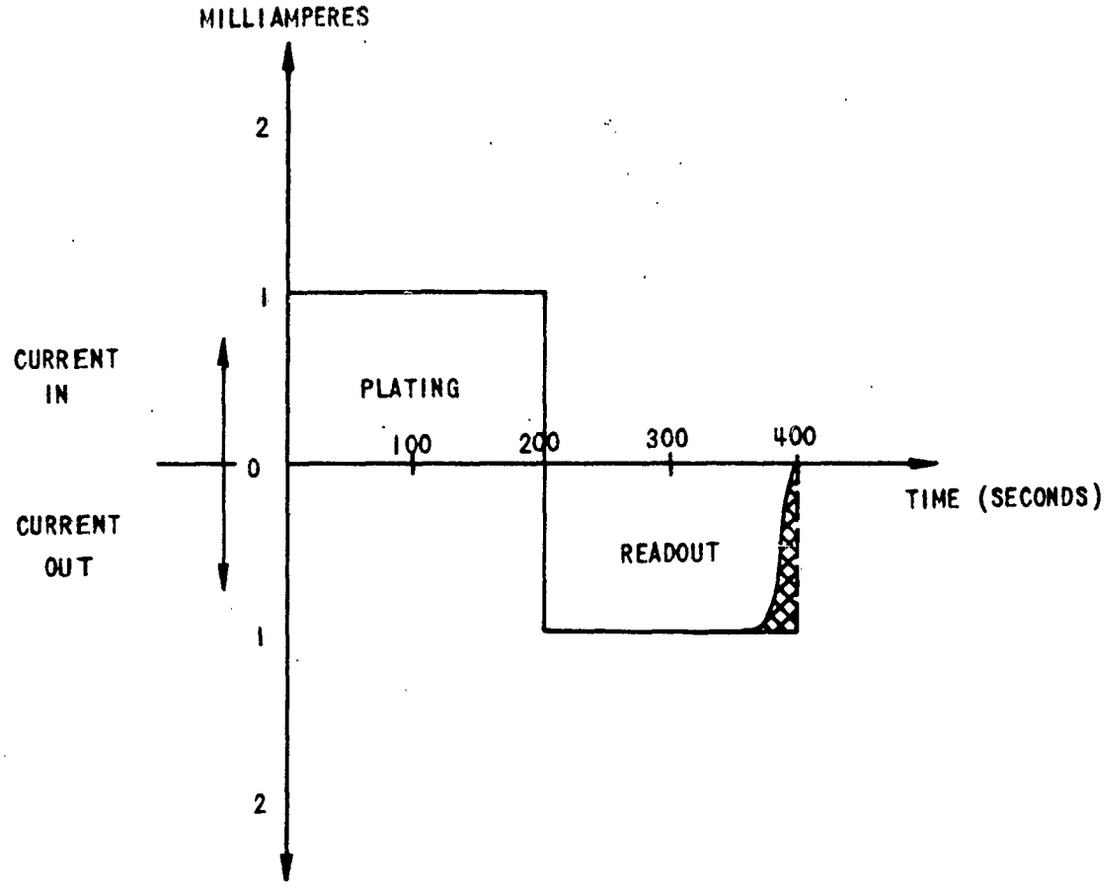
VII. REFERENCE

Mrgudich, J. N., Electrochem. Soc., 107, 475 (1960).



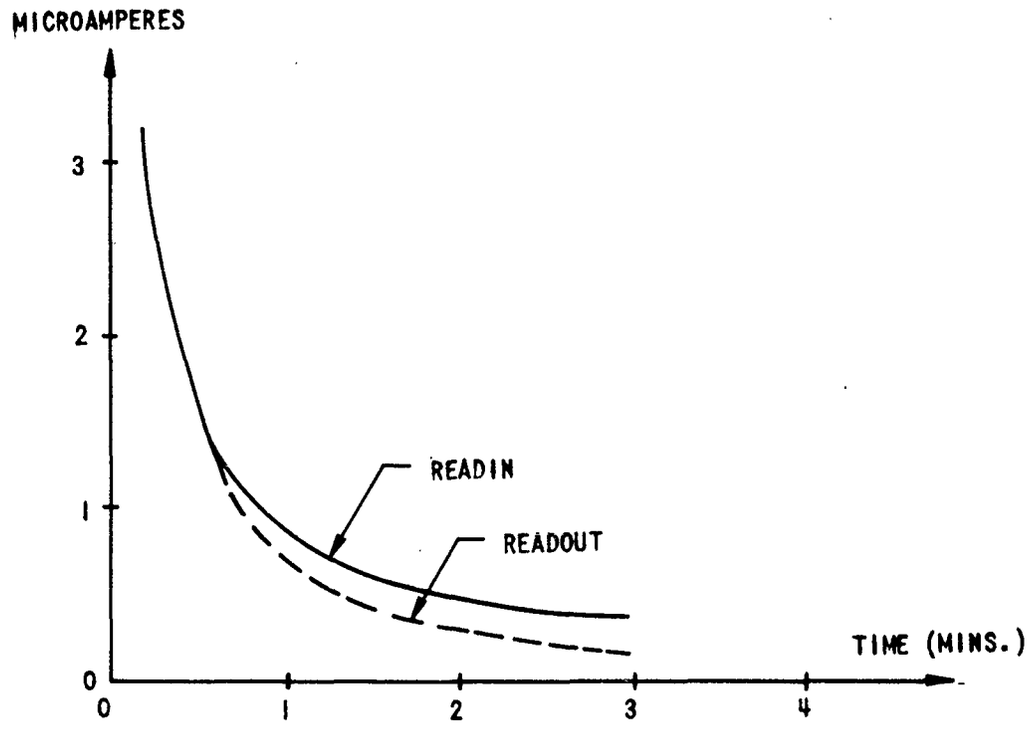
AN IONIC MEMORY DEVICE. READIN CONSISTS OF PLATING SILVER ONTO THE PLATINUM. READOUT CONSISTS OF REVERSING THE VOLTAGE AND READING THE CURRENT ASSOCIATED WITH REMOVAL OF THIS PLATED SILVER.

FIGURE 1



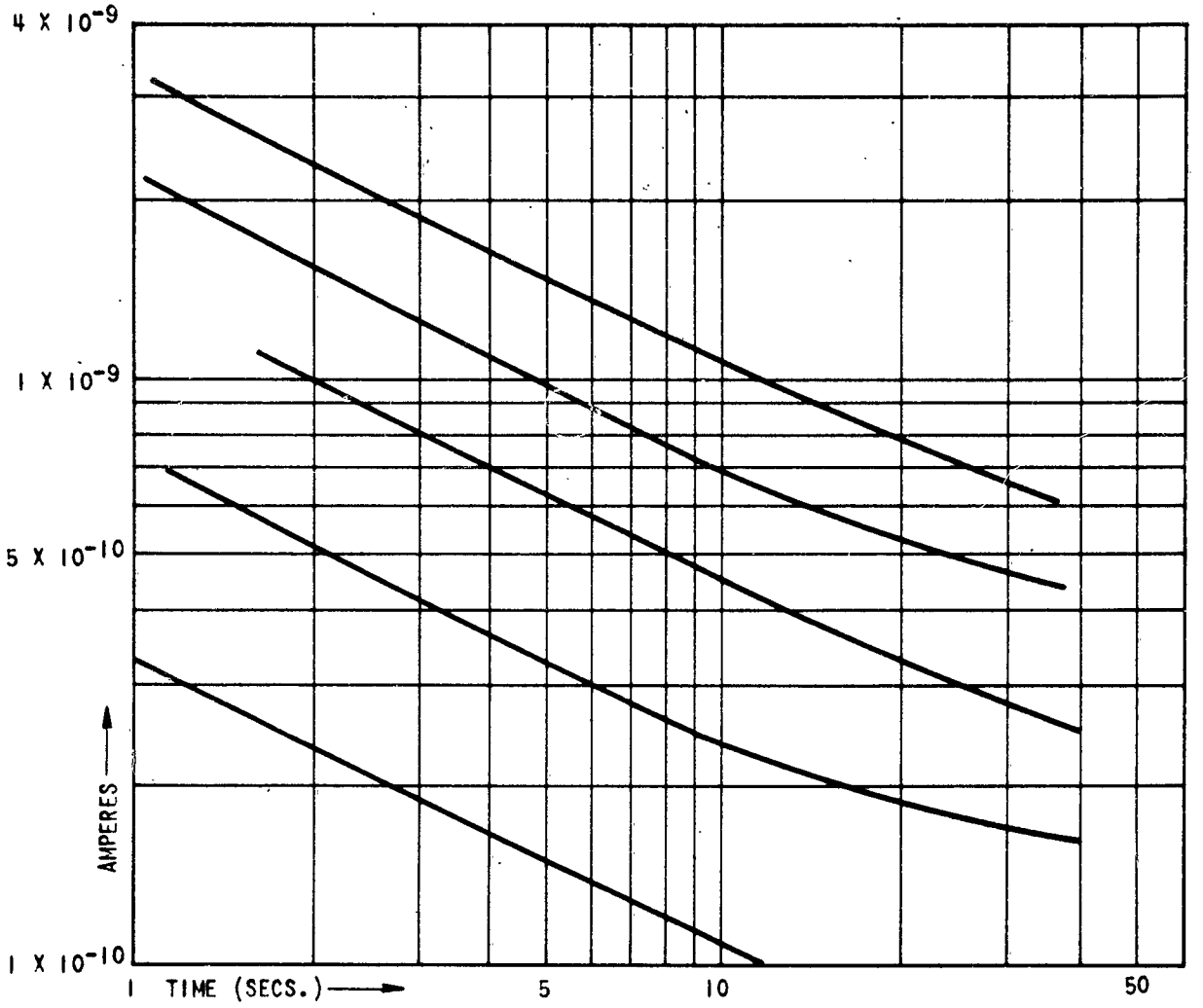
READOUT NOT QUITE EQUAL TO PLATING "READIN".
AT PLATING VOLTAGES GREATER THAN 0.14 VOLT.

Figure 2



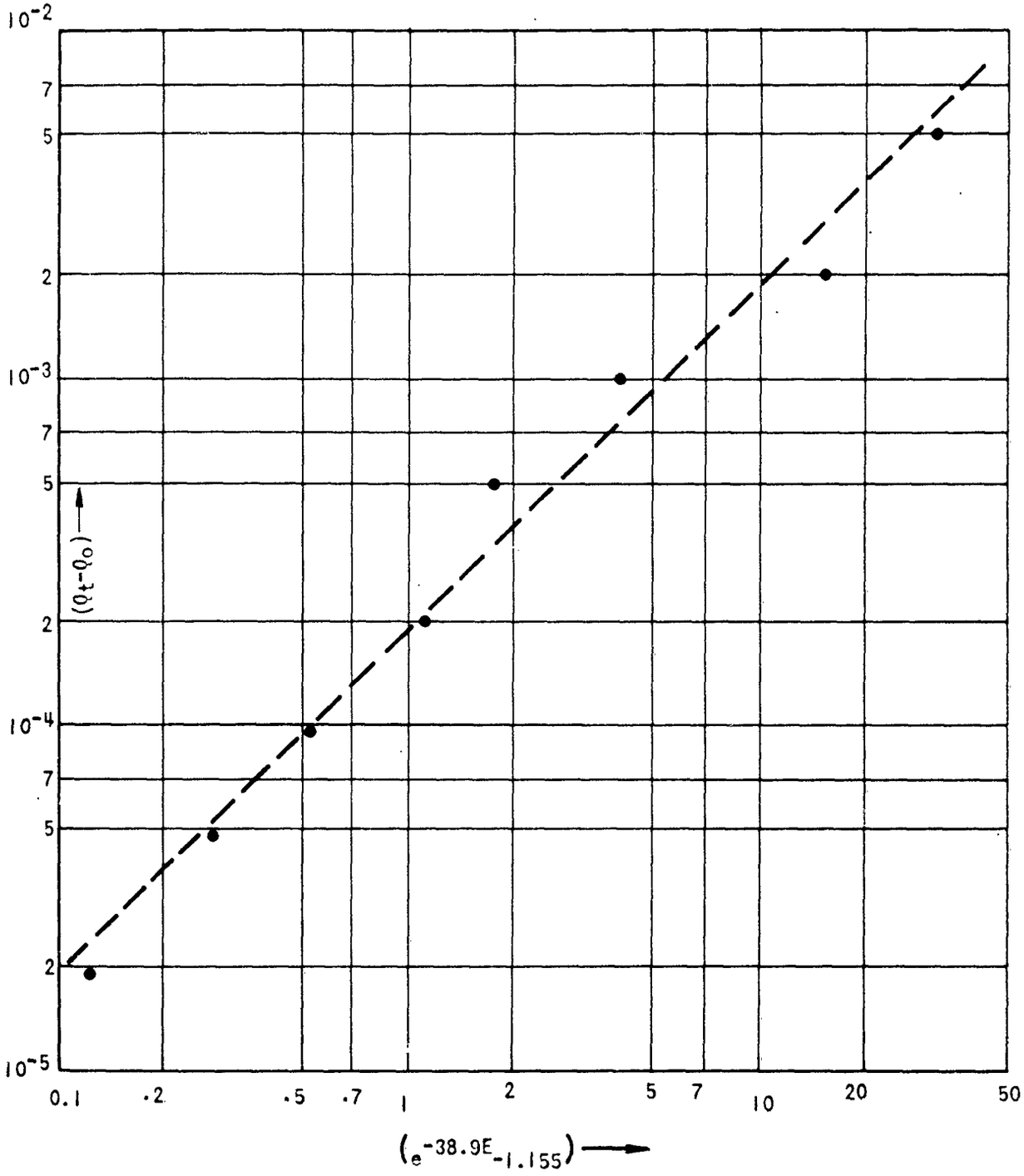
READIN AND READOUT TRANSIENTS AT 0.06 VOLT.
NOTE REDUCED ORDINATE SCALE COMPARED TO FIGURE 2.

FIGURE 3



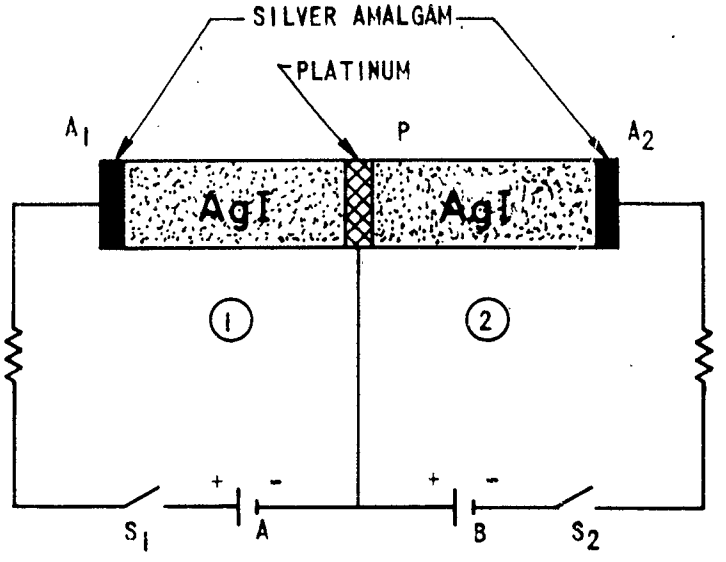
ILLUSTRATING LINEAR RELATIONSHIP BETWEEN
LOG CURRENT AND LOG TIME. SLOPE =-1/2.

Figure 4



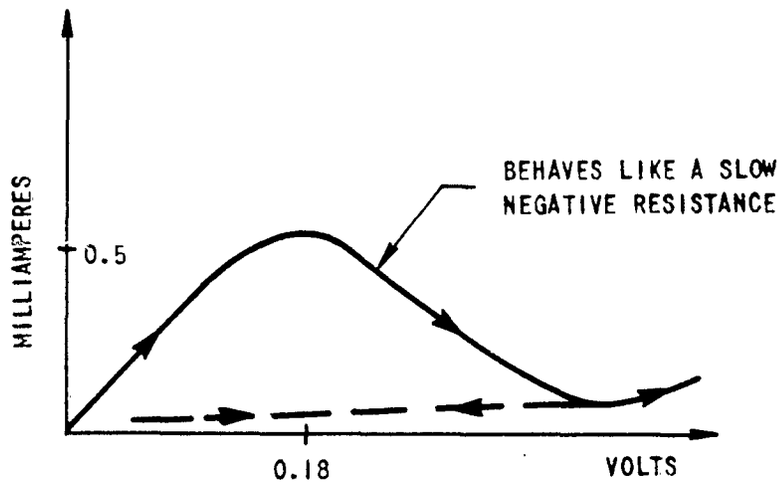
OBSERVED LINEARITY INDICATES VALIDITY OF USING CONCENTRATION-CELL CONCEPT.

FIGURE 5



A TIME-DELAY DEVICE. CURRENT IN CIRCUIT 1 WILL EVENTUALLY RESULT IN CURRENT IN CIRCUIT 2.

FIGURE 6



CURRENT-VOLTAGE RELATIONSHIP IN SILVER SULFIDE BETWEEN PLATINUM ELECTRODES.

FIGURE 7

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(DA Task 3A99-25-003-01) Unclassified report

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2. Silver Iodide
3. Devices, Ionic

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